



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number: 0 623 553 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 94107149.0

(51) Int. Cl.5: C01B 15/10, C11D 3/39,
C11D 17/00

(22) Date of filing: 06.05.94

(30) Priority: 06.05.93 JP 105551/93
06.05.93 JP 105552/93
23.06.93 JP 152245/93

(43) Date of publication of application:
09.11.94 Bulletin 94/45

(84) Designated Contracting States:
BE DE FR GB IT SE

(71) Applicant: MITSUBISHI GAS CHEMICAL
COMPANY, INC.
5-2, Marunouchi 2-chome
Chiyoda-Ku
Tokyo, 100 (JP)

(72) Inventor: Kokubo, Jun, Mitsubishi Gas Kagaku
Yokkaichi Works,
Hinagahigashi 2-chome
Yokkaichi-shi, Miye Pref. (JP)
Inventor: Hiro, Yasuo, Mitsubishi Gas Kagaku
Yokkaichi Works,
Hinagahigashi 2-chome
Yokkaichi-shi, Miye Pref. (JP)
Inventor: Hisano, Katsuhiko, Mitsubishi Gas
Kagaku
Yokkaichi Works,
Hinagahigashi 2-chome
Yokkaichi-shi, Miye Pref. (JP)
Inventor: Watanabe, Susumu, Mitsubishi Gas
Kagaku
Yokkaichi Works,
Hinagahigashi 2-chome
Yokkaichi-shi, Miye Pref. (JP)

(74) Representative: Goddar, Heinz J., Dr. et al
FORRESTER & BOEHMERT
Franz-Joseph-Strasse 38
D-80801 München (DE)

(54) Stabilized particle of sodium percarbonate.

(57) A stabilized sodium percarbonate particle includes a sodium percarbonate particle having at least one coating layer thereon, wherein the at least one coating layer includes (a) a silicate; (b) magnesium sulfate; and (c) an alkali metal salt selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates and alkali metal sulfate. The present sodium percarbonate particle is good in solubility and is excellent in its formulation stability with detergent.

EP 0 623 553 A1

FIELD OF THE INVENTION

The present invention relates to a particle of sodium percarbonate which has high storage stability and which is useful for a synthetic detergent for family use containing a bleach component, etc., and a method 5 for its preparation.

BACKGROUND OF THE INVENTION

It is well known that hydrogen peroxide, such as in sodium percarbonate and sodium perborate, is 10 formulated in a powdery detergent composition (synthetic detergent for family use) as a bleach component. Hydrogen peroxide, such as in sodium percarbonate and sodium perborate, dissolves in laundry to perform bleaching action.

In this case, the solubility rate of sodium perborate at a low temperature is small, so it is not preferable 15 for a bleach component formulated in a detergent in Japan, where cold water or tepid water is used in laundry. On the other hand, the solubility rate of sodium percarbonate at a low temperature is high, and the bleaching effect is sufficiently performed, so the need for it has increased rapidly in recent years.

However, sodium percarbonate is relatively sensitive to water content and is easily dissolved at room 20 temperature by water content in a detergent composition or by moisture or water content in the air. Further, there is a case that substances such as zeolites or enzymes, which accelerate the dissolution of sodium percarbonate, are contained in detergent composition, and it is dissolved by contacting with the substances.

Thus, until this time, several methods in which the dissolution of sodium percarbonate is prevented or 25 prohibited to obtain stabilized sodium percarbonate have been suggested. For example, there are methods in which stability is performed by adding a stabilizer such as sodium metasilicate, a magnesium compound and a chelating agent at the time of crystallization; by adding additives such as a binder or phosphates at the time of wet granulation; and by coating a dried surface of sodium percarbonate.

Among these, the third method (that is, the method in which a particle of sodium percarbonate is coated by several kinds of coating agents) is the most powerful method.

As the coating agent, a salt of alkaline earth metal or a mixture of sodium carbonate and sodium sulfate, etc., are suggested.

30 As the method in which a particle is coated with an alkaline earth metal salt, the method described in Japanese Patent Publication Sho 57-7081 is known. This method is the method in which the surface of sodium percarbonate is catalytically reacted with an alkaline earth metal salt solution, and a membrane comprising an alkaline earth metal carbonate is formed on the surface of the sodium percarbonate. This method certainly can raise somewhat the stability of sodium percarbonate, but there are two problems as 35 described below.

One problem is that when sodium carbonate in sodium percarbonate is reacted with an alkaline earth metal salt, the hydrogen peroxide which is liberated decomposes at the time of drying, so the effective component of sodium percarbonate decreases.

Another problem is that by the production of an insoluble alkaline earth metal carbonate, the solubility 40 rate becomes extremely small, so it is difficult to use.

On the other hand, in case of the method in which a particle is coated with a mixed salt of sodium carbonate and sodium percarbonate or sodium sulfonate (Japanese Patent Publication Sho 58-24361), the solubility is relatively good, but the stability of the formulation with detergent does not reach a practical level, although it improves somewhat as compared with uncoated sodium percarbonate.

45 SUMMARY OF THE INVENTION

A problem that the present invention is directed to solving is to develop a particle of sodium percarbonate which satisfies both stability and solubility requirements at the same time.

50 As a result of extensive research, it has now been found that a stabilized sodium percarbonate particle which comprises a sodium percarbonate particle having at least one coating layer thereon, wherein the at least one coating layer comprises a silicate, magnesium sulfate, and an alkali metal salt selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates and alkali metal sulfates, has a fast solubility and good formulation stability with detergent, and the inventors thus accomplished the present 55 invention.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, the present invention will be described in more detail.

- Coating of sodium percarbonate is conducted as follows. That is, on a sodium percarbonate particle, an aqueous solution of a silicate or a mixed aqueous solution of a silicate and an alkali metal carbonate is sprayed and dried to form a first coating layer, then an aqueous solution of magnesium sulfate independently or a mixed aqueous solution of magnesium sulfate and an alkali metal carbonate or sulfate is sprayed and dried to form a second coating layer.

- Further, on a sodium percarbonate particle, the coating layer may be formed by spraying the sodium percarbonate particle simultaneously using different nozzles and drying the above aqueous solutions.

When the order of spraying is reversed, i.e., at first, a solution containing magnesium sulfate is sprayed, then a solution of a silicate and a solution of an alkali metal carbonate is sprayed, the thus obtained sodium percarbonate particle has a decreased amount of active oxygen.

- Further, on a sodium percarbonate particle, the coating layer may be formed by spraying an aqueous solution of a silicate, an aqueous solution of magnesium sulfate and an aqueous solution containing an alkali metal bicarbonate or sulfate simultaneously or sequentially using different nozzles and drying.

Sodium percarbonate used in the present invention is obtained by cohesive-granulating, using a miscible-type granulator, sodium percarbonate (water content of 6-15 %) produced by reacting, crystallizing and dehydrating using a known method, with a binder, then rectifying using an extruder and drying.

- Further, sodium percarbonate which is produced by mixing wet powdery sodium percarbonate with recovered sodium percarbonate partially containing a coating agent component, such as a silicate component, magnesium sulfate component or alkali metal sulfate component recovered from granulation steps and/or coating steps, etc., then granulating using the above-mentioned procedure, is preferably used.

- The composition ratio of the wet powdery sodium percarbonate and the recovered sodium percarbonate is preferably within the ratio from 50:50 to 99:1. Particularly, when the recovered sodium percarbonate is finely powdered such that the diameter of the recovered sodium percarbonate is 300 μm and below, preferably from 5 to 100 μm , the stability of sodium percarbonate further increases.

- The sodium percarbonate particle used in the present invention which is at the post-granulation step and pre-coating step is usually from 300 to 3000 μm , preferably from 300 to 2000 μm , more preferably from 500 to 1000 μm in diameter.

As the silicate as a coating agent, a sodium salt, such as sodium orthosilicate, sodium metasilicate, water-glass No. 1, No. 2, No. 3, etc., can be used. Among these, water-glasses are liquid and are preferably used in view of convenience.

- The coating amount of the silicate is preferably 0.01 mole to 0.06 mole based on SiO_2 per mole of uncoated sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 3/2 \text{H}_2\text{O}_2$; molecular weight: 157). That is, the silicate is coated in an amount of 0.3 parts to 2.2 parts based on SiO_2 (molecular weight: 60.3) per 100 parts of sodium percarbonate. In the case that the coating amount of the silicate is too small, the coverage of the coating decreases, and the formulation stability with detergent becomes insufficient. In contrast, in the case where the coating amount of the silicate is too large, the solubility rate becomes slow.

- As the alkali metal bicarbonate as a coating agent, sodium bicarbonate, potassium bicarbonate, lithium bicarbonate, etc., may be used.

Further, these can be used in combination. Among these, sodium carbonate is most preferable from the viewpoint of economical efficiency.

- The coating amount of the alkali metal bicarbonate is preferably 0.05 mole to 0.25 mole per mole of uncoated sodium percarbonate. That is, in the case of sodium bicarbonate (molecular weight: 84), the alkali metal bicarbonate is present in an amount of 2.7 to 13.4 parts per 100 parts of sodium percarbonate (molecular weight: 157). In the case of 0.05 mole of alkali metal bicarbonate and below per mole of uncoated sodium percarbonate, the formulation stability with detergent is insufficient. In contrast, in the case of 0.25 mole of alkali metal bicarbonate and more per mole of uncoated sodium percarbonate, not only does the solubility rate decrease, but also economical efficiency is not preferable.

As the alkali metal carbonate as a coating agent, sodium carbonate, potassium carbonate, lithium carbonate, etc., may be used. Further, these can be used in combination. Among these, sodium carbonate is most preferable from the viewpoint of economical efficiency.

- The coating amount of the alkali metal carbonate is preferably 0.075 mole to 0.18 mole per mole of uncoated sodium percarbonate. That is, in the case of sodium carbonate (molecular weight: 106), the alkali metal carbonate is from 5 parts to 12 parts per 100 parts of sodium percarbonate. In case that the coating amount of the alkali metal carbonate is 0.075 mole and less, the formulation stability with detergent decreases. In contrast, in the case of an alkali metal carbonate coating amount of 0.18 mole and more, not

only does the solubility rate become slow, but also it is not preferable in view of economical efficiency.

As the alkali metal sulfate as a coating agent, sodium sulfate, potassium sulfate, lithium sulfate, etc., may be used. Further, these can be used in combination. Among these, sodium sulfate is most preferable from the viewpoint of economical efficiency.

- 5 The coating amount of the alkali metal sulfate is preferably from 0.05 mole to 0.20 mole per mole of uncoated sodium percarbonate. That is, in the case that the alkali metal sulfate is sodium sulfate anhydride (molecular weight: 142), it is present in an amount of from 4.5 parts to 18 parts per 100 parts of sodium percarbonate. In case that coating amount of the alkali metal sulfate is 0.05 mole and less, the formulation stability with detergent insufficient. In contrast, in case of an alkali metal sulfate coating amount of 0.2 mole and more, not only does the solubility rate become slow, but it is also not preferable in view of economical efficiency.
- 10

In the present invention, as the alkali metal salt, alkali metal sulfate is preferably used in combination with alkali metal bicarbonate. As the alkali metal sulfate and alkali metal bicarbonate, the above-mentioned compounds can be used, preferably, sodium sulfate and sodium bicarbonate.

- 15 The coating amount is desirably from 0.05 mole to 0.2 mole of alkali metal sulfate and from 0.04 mole to 0.17 mole of alkali metal bicarbonate per mole of uncoated sodium percarbonate.

The coating amount of magnesium sulfate is preferably from 0.006 mole to 0.06 mole per mole of uncoated sodium percarbonate. That is, magnesium sulfate (molecular weight: 120.3) is coated in an amount of from 0.45 parts to 4.5 parts per 100 parts of sodium percarbonate. In the case that coating amount of magnesium sulfate is 0.006 mole and less, the formulation stability with detergent becomes insufficient. In contrast, in the case of a magnesium sulfate coating amount of 0.06 mole and more, the solubility rate becomes slow.

- 20
- 25 The ratio of each coating agent is not limited, as long as it is within the range described in the specification and recited in the claims of the present application. Usually, the ratio of the alkali metal salt : silicate : magnesium sulfate is within the range from 1:0.03:0.02 to 1:1.2:1.2, preferably, from 1:0.1:0.1 to 1:0.4:0.4, based on the mole ratio.

In particular, when an alkali metal bicarbonate is used as the alkali metal salt, the ratio of the alkali metal bicarbonate : silicate : magnesium sulfate is usually within the range from 1:0.03:0.024 to 1:1.2:1.2, preferably from 1:0.1:0.1 to 1:0.2:0.2, based on the mole ratio.

- 30 When an alkali metal carbonate is used as the alkali metal salt, the ratio of alkali metal carbonate : silicate : magnesium sulfate is usually within the range from 1:0.05:0.03 to 1:0.8:0.8, preferably from 1:0.1:0.1 to 1:0.4:0.4, based on the mole ratio.

When an alkali metal sulfate is used as the alkali metal salt, the ratio of alkali metal sulfate : silicate : magnesium sulfate is usually within the range from 1:0.05:0.03 to 1:1.2:1.2, preferably from 1:0.1:0.1 to 1:0.2:0.2, based on the mole ratio.

When a combination of an alkali metal sulfate and an alkali metal bicarbonate is used as the alkali metal salt, the ratio of alkali metal sulfate : silicate : magnesium sulfate : alkali metal bicarbonate is usually within the range from 1:0.05:0.03:0.2 to 1:1.2:1.2:0.85, preferably from 1:0.1:0.1:0.4 to 1:0.2:0.2:0.85, based on the mole ratio.

- 40 Additionally, besides the above-mentioned coating agent, a chelating agent or stabilizer, such as ethylenediaminetetraacetic acid (EDTA) or salts thereof (EDTA-4Na, etc.), nitrilotriacetic acid, etc., may be used in combination with the coating agent.

Particularly, when a chelating agent is added into a mixture of magnesium sulfate and sodium bicarbonate, crystallization does not occur at all. That is, if a chelating agent is not added, depending upon the concentration of the aqueous solution, there is a case that crystallization appears partially several days after the preparation of the liquid.

When sodium percarbonate is coated, the solvent of these coating agents is selected from solvents which dissolve the coating agent, and water, which has high solubility and is safe and cheap, is most preferable.

- 50 The concentration of the coating agent at the time of spraying may be not more than the saturated concentration of solubility at the temperature in use; however, when the concentration is too small, not only does it require time to dry, but also the calories of water vaporized becomes large, and thus a low concentration is not preferable from the viewpoint of economical efficiency. On the other hand, when the concentration is too high, crystallization may occur and block tubes or nozzles and thus a high concentration is not preferable. Thus, the liquid concentration of a silicate is preferably from 0.5 % by weight to 9 % by weight, more preferably from 1 % by weight to 6 % by weight, based on SiO₂. On the other hand, the liquid concentration of magnesium sulfate is preferably from 0.2 % by weight to 25 % by weight, more preferably from 0.5 % by weight to 20 % by weight. The liquid concentration of an alkali metal sulfate is
- 55

preferably from 3 % by weight to 20 % by weight, more preferably from 5 % by weight to 15 % by weight. The liquid concentration of an alkali metal bicarbonate is preferably from 3 % by weight to 9 % by weight, more preferably from 5 % by weight to 8 % by weight.

5 The liquid concentration of an alkali metal carbonate is preferably from 5 % by weight to 20 % by weight, more preferably from 7 % by weight to 15 % by weight.

The temperature of the sodium percarbonate at the time of spray-drying is preferably from 40 to 95 °C, more preferably from 50 to 90 °C. In case that the temperature of the sodium percarbonate is too low, particles of sodium percarbonate agglomerate, and the embodiment is not preferable. On the other hand, in the case that the temperature of the sodium percarbonate is too high, sodium percarbonate tends to decompose, and it is hard to make a uniform coating because of the growth of crystals of the coating agent.

10 The present sodium percarbonate particle has an excellent solubility rate and has excellent formulation stability with detergent. The present sodium percarbonate is uniformly coated on its surface with a silicate, magnesium sulfate, and at least one of an alkali metal carbonate, bicarbonate, and sulfate and/or a reaction product thereof, and can show stabilizing action by cutting off water or another kicker. By using the 15 combination of the components used in the present invention as a coating agent, a particularly excellent stabilizing effect is obtained.

The sodium percarbonate particle coated in accordance with the present invention is not only excellent in its formulation stability with a zeolite or detergent which has a characteristic of a kicker, but also has an excellent solubility rate and can be used in low temperature laundry.

20 Hereinafter the present invention will be explained in more detail using examples and comparative examples. The present invention is not limited to these examples. The use of % in the examples means % by weight, unless otherwise described expressly.

EXAMPLE 1

25

300 g of sodium percarbonate having a mean diameter of 500 µm (active oxygen 14.4 %) was placed on a multipore plate of a fluid dry coater (Yamato Scientific Co., Ltd., PULVIS MINI BED), then air at 0.25 m³/min was sent to make fluidization. Thereafter, by warming inlet air, the temperature of the fluidizing sodium percarbonate was raised to 75 °C. After the temperature was steady at 75 °C, to keep it in a fluid state, 225 g of an aqueous solution of water-glass No. 1 (water-glass No. 1 concentration of 2 wt% based on SiO₂) was sprayed from a spray nozzle located 10 cm above the multipore plate over 39 minutes at a flow rate of 7.5 g/min. After spray completion, the sample was dried for 5 minutes, and the first coating layer was thereby formed. Then, after a change of the nozzle, 500 g of a mixed aqueous solution of magnesium sulfate and sodium bicarbonate (MgSO₄ concentration of 0.9 wt%, NaHCO₃ concentration of 35 6.6 wt %) was sprayed at a flow rate of 7.5 g/min over 67 minutes. Similarly as the above, after completion of the spraying, the sample was dried for 5 minutes, and the second coating layer was thereby formed. In the coating, the temperature of the sodium percarbonate was controlled from 73 to 77 °C. The coating amount of each component as solids content was as follows:

- 35 Water-glass No. 1 (SiO₂) in the first coating layer
 40 —4.5 g (1.5 % of the sodium percarbonate to be coated)
 Magnesium sulfate in the second coating layer
 —4.5 g (1.5 % of the sodium percarbonate to be coated)
 Sodium bicarbonate in the second coating layer
 —33.0 g (11 % of the sodium percarbonate to be coated).
 45 After cooling, the coated sodium percarbonate was taken out and no aggregate was observed.
 Useful oxygen of the obtained sodium percarbonate analyzed to 12.5 %.
 From this value, decomposition of the active oxygen at coating time was extremely small, with the coating agent being coated the same as the theoretical value. (Theoretical value: 14.4 % × 1 / (1 + 0.14) = 12.6 %)
 50 Further, coated sodium percarbonate was mixed with a zeolite and detergent to investigate the storage stability test. The result together with the result of the solubility rate is shown in Table 1. Formulation stability was very good, and great improvement of stability as compared with uncoated sodium percarbonate described below was recognized.

55 Solubility test

5 g of sodium percarbonate particle was charged into 1 l of water and stirred at 200 rpm. The time for the particle to dissolve completely was measured by the electrical conductance method.

Storage stability test 1

5 1 g of synthetic zeolite 4A powder which was sufficiently absorbed with moisture for 1 day at 30 °C, relative humidity of 80 %, and 1 g of sodium percarbonate were charged into a polyethylene bag (Trade name: UNI PACK A-4, Seisan Nippon Sya Co., Ltd., water permeable) and mixed sufficiently. The mixture stood for 4 days at 30 °C and a relative humidity of 80 %, and active oxygen of pre- and post-storage was analyzed, and formulation stability with a zeolite was investigated.

Storage stability test 2

10 To 1300 g of commercially available compact detergents (containing a zeolite and enzyme, etc.), 200 g of coated or uncoated sodium percarbonate (13.3 % against the detergent) was homogeneously mixed, put into carton board box, and then sealed with vinyl tape. The mixture was stored in a constant temperature bath for 21 days at 30 °C and a relative humidity of 80 %. The active oxygen amount of the samples was
15 determined by sodium thiosulfate precipitation. The residual rate of active oxygen was calculated according to the following formula. Residual rate of active oxygen (%) = (active oxygen at post-storage/active oxygen at pre-storage) × 100

EXAMPLE 2

20 Coated sodium percarbonate was obtained using the same procedures as in Example 1, except that potassium bicarbonate was used instead of sodium bicarbonate as a coating agent.

| | |
|---|---|
| Potassium bicarbonate: | 33.0 g (11.0 % of sodium percarbonate to be coated) |
| Water-glass No. 1 (as SiO ₂): | 4.5 g (1.5 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 4.5 g (1.5 % of sodium percarbonate to be coated) |

25 Active oxygen of the obtained sodium percarbonate analyzed to 12.6 %.
30 This value shows that without decomposing the active oxygen at the coating time, the coating agent was coated the same as the theoretical value. Further, solubility was investigated using the same procedure as in Example 1, and it was found that the sample dissolved by 2.5 minutes.

35 Formulation stability was investigated in the same manner as Example 1, and it was good. The result is shown in Table 1.

EXAMPLE 3

40 Coated sodium percarbonate was obtained using the same procedures as in Example 1, except that sodium metasilicate was used instead of water-glass No. 1 as a coating agent, the coating amount was changed, and a chelating agent corresponding to 0.5 % of the amount of the coating was added to the mixed solution of magnesium sulfate and sodium bicarbonate in order to stabilize the solution.

| | |
|---|---|
| Sodium bicarbonate: | 33.0 g (11.0 % of sodium percarbonate to be coated) |
| Sodium meta silicate : | 3.0 g (1.0 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 4.5g (1.5 % of sodium percarbonate to be coated) |
| Ethylenediaminetetraacetic acid tetrasodium salt: | 1.5g(1.5 % of sodium percarbonate to be coated). |

45 Active oxygen of the obtained sodium percarbonate, solubility and formulation stability were investigated, solubility was excellent, and formulation stability was good. The results are shown in Table 1.

The mixed solution of magnesium sulfate, sodium bicarbonate and chelating agent was stable and did not give any precipitate after storing a day.

EXAMPLE 4

55 12 kg of sodium percarbonate having a mean diameter of 500 μm (active oxygen: 14.4 %) was placed on a multipore plate of a fluid drying apparatus (Fuji Paudal Co., Ltd., "MIDGET-DRYER"), then air at 3.2 m³/min was sent to make fluidization. Thereafter, by warming inlet air to from 120 to 150 °C, the

temperature of the fluidizing sodium percarbonate was raised to 75 °C. After the temperature was steady at 75 °C, to keep it in a fluid state, a mixed solution of sodium bicarbonate and magnesium sulfate (Sodium bicarbonate concentration of 8 wt%, magnesium sulfate of 1 wt%) and an aqueous solution of sodium metasilicate (1.2 wt% based on SiO₂) was sprayed simultaneously from different spray nozzles located 40 cm above the multipore plate.

Spraying of 12 kg of the mixed solution of sodium bicarbonate and magnesium sulfate took 150 minutes at a speed of 80 g/min. On the other hand, spraying of 10 kg of the aqueous solution of sodium metasilicate took 150 minutes at a speed of 67 g/min., and the coating finished at almost the same time. The temperature during the coating was controlled from 73 to 77 °C. After completion of the coating, heated air continued to be sent for 5 minutes to dry. Next, heating from the air heater finished, and the sample was cooled with a cool air flow. After cooling, the coated sodium percarbonate was taken out, and no aggregate was observed.

The coating amount of each component as solids content was as follows:

| | | |
|----|--|---|
| 15 | NaHCO ₃ : Sodium metasilicate (SiO ₂): Magnesium sulfate: | 0.96 kg (8.0 % of the sodium percarbonate to be coated) 0.12 kg (1.0 % of the sodium percarbonate to be coated) 0.12 kg (1.0 % of the sodium percarbonate to be coated) |
|----|--|---|

20 Active oxygen of the obtained sodium percarbonate, solubility and formulation stability were investigated. The results are shown in Table 1.
 Solubility and formulation stability in case of simultaneous spraying were both excellent as in the case of multi-spraying of Examples 1, 2 and 3.

25 EXAMPLE 5

Coated sodium percarbonate was obtained using the same procedures as in Example 4, except that to the mixed solution of magnesium sulfate and sodium bicarbonate, EDTA-4Na as a chelating agent was added in an amount of 0.5 % corresponding to the coating amount, the coating amount was changed, and water-glass No. 1 was used instead of sodium metasilicate.

The spray time of the two liquids was finished after about 188 minutes. Active oxygen of the obtained sodium percarbonate, solubility and formulation stability were investigated. The results are shown in Table 1.

| | | |
|----|---|--|
| 35 | NaHCO ₃ : | 1.2 kg (10.0 % of the sodium percarbonate to be coated) |
| | Water-glass No. 1 (SiO ₂): | 0.15 kg (1.25 % of the sodium percarbonate to be coated) |
| 40 | Magnesium sulfate: | 0.15 kg (1.25 % of the sodium percarbonate to be coated) |
| | Ethylenediaminetetraacetic acid tetrasodium salt: | 1.5g(1.5 % of sodium percarbonate to be coated) |

45 As can be seen from Table 1, sodium percarbonate produced according to the Examples of the present invention was excellent in solubility (time required to dissolve completely was fast, i.e., from 2 to 2.5 min.), and formulation stability with detergent was good (only 10 % decomposition even after 21 days storage) and found to have a balanced good property.

50 COMPARATIVE EXAMPLE 1

Active oxygen, solubility and formulation stability of uncoated sodium percarbonate which was used as a raw material in the present invention were investigated. The results are shown in Table 1 for comparison.

55 COMPARATIVE EXAMPLE 2

Coated sodium percarbonate was obtained using the same procedures as in Example 1, except that the spraying of the second layer was not conducted.

Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 1. The formulation stability was only a little better than in the uncoated sample of COMPARATIVE EXAMPLE 1 and did not show a great improvement like in Example 1. Further, the solubility was rather bad, which may have been because of the use of only one component of 5 SiO_2 .

COMPARATIVE EXAMPLE 3

Coated sodium percarbonate was obtained using the same procedures as in Example 1, except that the 10 spraying of the first layer was not conducted.

| | |
|------------------------|---|
| Potassium bicarbonate: | 33.0 g (11.0 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 4.5 g (1.5 % of sodium percarbonate to be coated) |

15 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 1. Although the solubility was good, the formulation stability did not show a great improvement like in Example 1.

COMPARATIVE EXAMPLE 4

20 300 g of sodium percarbonate having a mean diameter of 500 μm (Active oxygen: 14.4 %) was placed on a multipore plate of a fluid dry coater (Yamato Scientific Co., Ltd., PULVIS MINI BED), then air at 0.25 m³/min was sent to make fluidization. Thereafter, by warming inlet air, the temperature of the fluidizing 25 sodium percarbonate was raised to 75 °C. After the temperature was steady at 75 °C, to keep it in a fluid state, 180 g of an aqueous solution of magnesium chloride (10 % concentration of magnesium chloride) was sprayed from a spray nozzle located 10 cm above the multipore plate over 36 minutes at a flow rate of 5 g/min. After spray completion, the contents were removed from the apparatus, moved to a vacuum dryer, and dried for 4 hours at 50 °C under 3 mmHg.

25 30 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 1. The formulation stability did not show a great improvement like in Example 1. In particular, the formulation stability with a zeolite was low, like the uncoated sample in COMPARATIVE EXAMPLE 1.

30 35 Further, a great decrease of useful oxygen which was over the value of dilution by the coating agent was observed.

| | |
|---|---|
| Theoretical conc. of active oxygen: | $14.4 \% \times 1 / (1 + 0.06) = 13.6 \%$ |
| Actually measured conc. of active oxygen: | 12.9 % |

40 45 Also, the sample took 5 minutes to dissolve in COMPARATIVE EXAMPLE 4, so it is not applicable when laundry is conducted at a low temperature.

COMPARATIVE EXAMPLE 5

300 g of sodium percarbonate having a mean diameter of 500 μm (active oxygen: 14.4 %) was placed on a multipore plate of a fluid dry coater (Yamato Scientific Co., Ltd., PULVIS MINI BED), then air at 0.25 m³/min was sent to make fluidization. Thereafter, by warming inlet air, the temperature of the fluidizing sodium percarbonate was raised to 50 °C. After the temperature was steady at 50 °C, to keep it in a fluid state, 129 g of an aqueous solution of a mixed salt of sodium carbonate and sodium bicarbonate (sesquicarbonate) (8.6 % concentration of sodium carbonate, 3 % of sodium bicarbonate) was sprayed from a spray nozzle located 10 cm above the multipore plate over 26 minutes at a flow rate of 5 g/min. For 10 minutes after spray completion, only gas at the same temperature continued to be sent, and drying was completed. Then, the gas was changed to cool wind, and the sample was cooled to 30 °C. Then, the 50 55 coated sodium percarbonate was removed from the apparatus, and little aggregates were observed.

| | |
|---------------------|--|
| Sodium bicarbonate: | 3.9 g (1.3 % of sodium percarbonate to be coated) |
| Sodium carbonate: | 11.1 g (3.7 % of sodium percarbonate to be coated) |

5 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 1. The solubility was preferable, but the formulation stability did not show a great improvement like in Example 1.

COMPARATIVE EXAMPLE 6

10 Coated sodium percarbonate was obtained using the same procedures as in Example 1, except that the coating amount of water-glass No. 1 was 12.5 %, after formulation of the first coating layer, the second coating layer was formulated using only an aqueous solution of magnesium sulfate, without using sodium bicarbonate, and total coating amount was the same as in Example 1.

| | |
|--|---|
| Water-glass No. 1 (SiO ₂): | 37.5 g (12.5 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 4.5 g (1.5 % of sodium percarbonate to be coated) |

15 20 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 1.

Table 1

| | EXAMPLE | | | | | COMPARATIVE EXAMPLE | | | | | |
|-------------------------|---------|-----|-----|-----|-----|---------------------|-----|-----|-----|-----|-----|
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | 6 |
| Solubility (min.) | 2.5 | 2.5 | 2.0 | 2.0 | 2.5 | 1.5 | 3.5 | 1.5 | 5.0 | 2.5 | 9.0 |
| Storage Stability 1 (%) | 95 | 90 | 92 | 91 | 93 | 30 | 65 | 78 | 43 | 48 | 85 |
| Storage Stability 2 (%) | 92 | 88 | 90 | 90 | 91 | 50 | 59 | 70 | 75 | 64 | 70 |

EXAMPLE 6

25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 9245 9250 9255 9260 9265 9270 9275 9280 9285 9290 9295 9300 9305 9310 9315 9320 9325 9330 9335 9340 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 9445 9450 9455 9460 9465 9470 9475 9480 9485 9490 9495 9500 9505 9510 9515 9520 9525 9530 9535 9540 9545 9550 9555 9560 9565 9570 9575 9580 9585 9590 9595 9600 9605 9610 9615 9620 9625 9630 9635 9640 9645 9650 9655 9660 9665 9670 9675 9680 9685 9690 9695 9700 9705 9710 9715 9720 9725 9730 9735 9740 9745 9750 9755 9760 9765 9770 9775 9780 9785 9790 9795 9800 9805 9810 9815 9820 9825 9830 98

Active oxygen of the obtained sodium percarbonate analyzed to 12.6 %.

This shows that there was no decomposition of the active oxygen at the coating time, and that the coating agent was coated the same as the theoretical value.

(Theoretical value : $14.4\% \times 1 / (1 + 0.145) = 12.6\%$)

5 The obtained sodium percarbonate was dissolved by 2.5 min.

Further, coated sodium percarbonate was mixed with a zeolite and detergent to investigate the storage stability test. The result together with the result of the solubility rate is shown in Table 2. Formulation stability was very good, and a great improvement of stability as compared with uncoated sodium percarbonate described below was recognized.

10

EXAMPLE 7

Coated sodium percarbonate was obtained using the same procedures as in Example 6, except that amount of the coating was changed as set forth below.

15

| | |
|---|--|
| Sodium carbonate: | 24.8 g (8.3 % of sodium percarbonate to be coated) |
| Water-glass No. 1 (as SiO ₂): | 4.5 g (1.5 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 10.5 g (3.5 % of sodium percarbonate to be coated) |

20

Active oxygen of the obtained sodium percarbonate analyzed to 12.7 %.

This value shows that without decomposing the active oxygen at the coating time, the coating agent was coated the same as the theoretical value. Further, solubility was investigated using the same procedure as in Example 1, and it was found that the sample dissolved by 2.5 minutes.

25

Formulation stability was investigated in the same manner as Example 1, and it was good. The result is shown in Table 2.

EXAMPLE 8

30

Coated sodium percarbonate was obtained using the same procedures as in Example 6, except that potassium carbonate was used instead of sodium carbonate and that water-glass No. 3 was used instead of water-glass No. 1.

35

| | |
|---|---|
| Potassium carbonate: | 33.0 g (11.0 % of sodium percarbonate to be coated) |
| Water-glass No. 3 (as SiO ₂): | 6.0 g (2.0 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 4.5 g (1.5 % of sodium percarbonate to be coated) |

40

Active oxygen of the obtained sodium percarbonate, solubility and formulation stability were investigated, and the results are shown in Table 2.

EXAMPLE 9

45

12 kg of sodium percarbonate having a mean diameter of 500 μm (useful oxygen: 14.4 %) was placed on a multipore plate of a fluid drying apparatus (Fuji Paudal Co., Ltd., "MIDGET-DRYER"), then air at 3.2 m³/min was sent to make fluidization. Thereafter, by warming inlet air to from 120 to 150 °C, the temperature of the fluidizing sodium percarbonate was raised to 75 °C. After the temperature was steady at 75 °C, to keep it in a fluid state, a mixed solution of sodium carbonate and water-glass No. 1 (Na₂CO₃ concentration of 16.5 wt%, water-glass No. 1 of 3 wt% based on SiO₂) and an aqueous solution of magnesium sulfate (10 wt%) was sprayed simultaneously from different spray nozzles located 40 cm above the multipore plate.

50

Spraying of 8 kg of the mixed solution of sodium carbonate and water-glass No. 1 took about 76 minutes at a speed of 105 g/min. On the other hand, spraying of 1.8 kg of the aqueous solution of magnesium sulfate took 76 minutes at a speed of 23.7 g/min., and the coating finished at almost the same time. The temperature during the coating was controlled from 73 to 77 °C. After completion of the coating, heated air continued to be sent for 5 minutes so that the sample dried. Next, heating from the air heater finished, and the sample was cooled with a cool air flow. After cooling, the coated sodium percarbonate was taken out, and no aggregate was observed.

The coating amount of each component as solids content was as follows:

| | | |
|---|--|--|
| 5 | Na₂CO₃: Water-glass No. 1 (SiO ₂): Magnesium sulfate: | 1.32 kg (11.0 % of the sodium percarbonate to be coated) 0.24 kg (2.0 % of the sodium percarbonate to be coated) 0.18 kg (1.5 % of the sodium percarbonate to be coated) |
|---|--|--|

Active oxygen of the obtained sodium percarbonate, solubility and formulation stability were investigated. The results are shown in Table 2.

10 In the case of simultaneous spraying, solubility was a little bit slow as compared to the multi-spray case of Examples 6, 7 and 8.

EXAMPLE 10

15 Coated sodium percarbonate was obtained using the same procedures as in Example 9, except that a mixed solution of potassium carbonate and water-glass No. 3 was used instead of a mixed solution of sodium carbonate and water-glass No. 1.

| | | |
|----|--|--|
| 20 | Potassium carbonate: Water-glass No. 3 (as SiO ₂): Magnesium sulfate: | 1.32 Kg (11.0 % of sodium percarbonate to be coated) 0.24 Kg (2.0 % of sodium percarbonate to be coated) 0.18 Kg (1.5 % of sodium percarbonate to be coated) |
|----|--|--|

25 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated, and the results are shown in Table 2. As can be understood from Table 2, sodium percarbonate produced according to the Example of the present invention was shown to be good in solubility (necessary time for complete dissolution was from 2 to 2.5 minutes) and good in formulation stability (after 21 days storage, only 10 % was decomposed), and had a good balance in property.

COMPARATIVE EXAMPLE 7

Active oxygen, solubility and formulation stability of uncoated sodium percarbonate which was used as a raw material in the present invention were investigated. The results are shown in Table 2 for comparison.

COMPARATIVE EXAMPLE 8

Coated sodium percarbonate was obtained using the same procedures as in Example 6, except that the spraying of the second layer was not conducted.

| | | |
|----|---|--|
| 40 | Sodium carbonate: Water-glass No. 3 (as SiO ₂): | 33.0 g (11.0 % of sodium percarbonate to be coated) 6.0 g (2.0 % of sodium percarbonate to be coated) |
|----|---|--|

45 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 2. The formulation stability did not show a great improvement like in Example 1.

COMPARATIVE EXAMPLE 9

50 Coated sodium percarbonate was obtained using the same procedures as in Example 6, except that the spraying of the first layer was not conducted.

Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 2. The formulation stability did not show a great improvement like in Example 6. Further, a great decrease of useful oxygen which was over the value of dilution by the coating agent was observed.

| | |
|--|---|
| Theoretical conc. of active oxygen: Actually measured conc. of active oxygen: | $14.4 \% \times 1 / (1 + 0.015) = 14.2 \%$ 13.9% |
|--|---|

5

COMPARATIVE EXAMPLE 10

300 g of sodium percarbonate having a mean diameter of 500 μm (active oxygen: 14.4 %) was placed on a multipore plate of a fluid dry coater (Yamato Scientific Co., Ltd., PULVIS MINI BED), then air at 0.25 m³/min was sent to make fluidization. Thereafter, by warming inlet air, the temperature of the fluidizing sodium percarbonate was raised to 75 °C. After the temperature was steady at 75 °C, to keep it in a fluid state, 180g of an aqueous solution of magnesium chloride (10 % concentration of magnesium chloride was sprayed from a spray nozzle located 10 cm above the multipore plate over 36 minutes at a flow rate of 5 g/min. After spray completion, the contents were removed from the apparatus, moved to a vacuum dryer, and dried for 4 hours at 50 °C under 3 mmHg.

Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 2. The formulation stability did not show a great improvement like in Example 6. In particular, the formulation stability with a zeolite was low, like the uncoated sample in COMPARATIVE EXAMPLE 6.

20 Further, a great decrease of active oxygen which was over the value of dilution by the coating agent was observed.

25

| | |
|--|---|
| Theoretical conc. of active oxygen: Actually measured conc. of active oxygen: | $14.4 \% \times 1 / (1 + 0.06) = 13.6 \%$ 12.9 % |
|--|---|

Also, the sample took 5 minutes to dissolve in COMPARATIVE EXAMPLE 9, so it is not applicable when laundry is conducted at a low temperature.

30

COMPARATIVE EXAMPLE 11

300 g of sodium percarbonate having a mean diameter of 500 μm active oxygen: 14.4 %) was placed on a multipore plate of a fluid dry coater (Yamato Scientific Co., Ltd., PULVIS MINI BED), then air at 0.25 m³/min was sent to make fluidization. Thereafter, by warming inlet air, the temperature of the fluidizing sodium percarbonate was raised to 50 °C. After the temperature was steady at 50 °C, to keep it in a fluid state, 150g of an aqueous solution of a mixed salt of sodium carbonate and sodium sulfate (8.8 % concentration of sodium carbonate, 11.2 % of sodium sulfate) was sprayed from a spray nozzle located 10 cm above the multipore plate over 30 minutes at a flow rate of 5 g/min. For 10 minutes after spray completion, only gas at the same temperature continued to be sent, and drying was completed. Then, the 40 gas was changed to cool wind, and the sample was cooled to 30 °C. Then, the coated sodium percarbonate was removed from the apparatus, and little aggregates were observed.

45

| | |
|--------------------------------------|--|
| Sodium carbonate: Sodium sulfate: | 13.2 g (4.4 % of sodium percarbonate to be coated) 16.8 g (5.6 % of sodium percarbonate to be coated) |
|--------------------------------------|--|

Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 2. The solubility was preferable, but the formulation stability did not show a great improvement like in Example 6.

50

COMPARATIVE EXAMPLE 12

Coated sodium percarbonate was obtained using the same procedures as in Example 6, except that without using sodium carbonate, the first coating layer was formulated using only an aqueous solution of 55 water-glass No. 1.

| | |
|---------------------------------------|---|
| Water-glass No. 1 (SiO_2): | 39 g (13 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 4.5 g (1.5 % of sodium percarbonate to be coated) |

- 5 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 2.

Table 2

| | EXAMPLE | | | | | COMPARATIVE EXAMPLE | | | | | |
|-------------------------|---------|-----|-----|-----|-----|---------------------|-----|-----|-----|-----|------|
| | 6 | 7 | 8 | 9 | 10 | 7 | 8 | 9 | 10 | 11 | 12 |
| Solubility (min.) | 2.5 | 2.5 | 2.5 | 2.0 | 2.5 | 1.5 | 3.0 | 3.5 | 5.0 | 1.5 | 10.0 |
| Storage Stability 1 (%) | 90 | 90 | 89 | 91 | 90 | 30 | 67 | 35 | 43 | 48 | 84 |
| Storage Stability 2 (%) | 91 | 90 | 87 | 90 | 90 | 50 | 62 | 55 | 75 | 55 | 67 |

20 EXAMPLE 11

300 g of sodium percarbonate having a mean diameter of 500 μm (active oxygen: 14.4 %) was placed on a multipore plate of a fluid dry coater (Yamato Scientific Co., Ltd., PULVIS MINI BED), then air at 0.25 m³/min was sent to make fluidization. Thereafter, by warming inlet air, the temperature of the fluidizing 25 sodium percarbonate was raised to 75 °C. After the temperature was steady at 75 °C, to keep it in a fluid state, 105 g of an aqueous solution of sodium metasilicate (concentration of 2 wt%, based on SiO_2) was sprayed from a spray nozzle located 10 cm above the multipore plate over 21 minutes at a flow rate of 5 g/min. After spray completion, the sample was dried for 5 minutes, and the first coating layer was thereby formed. Then, after a change of the nozzle, 100 g of a mixed solution of magnesium sulfate and sodium 30 sulfate (magnesium sulfate of 4.2 wt%, sodium sulfate concentration of 15 wt%) was sprayed at a flow rate of 5 g/min over 20 minutes. After completion of the spraying, the sample was dried for 5 minutes, and the second coating layer was thereby formed. The temperature during coating was controlled from 73 to 77 °C. The coating amount of each component as solids content was as follows:

| | | |
|----|---|--|
| 35 | Sodium metasilicate in the first coating layer: | 2.1 g (as SiO_2 0.7% of the sodium percarbonate to be coated) |
| 40 | Magnesium sulfate in the second coating layer: | 4.2 g (1.4% of the sodium percarbonate to be coated) |
| | Sodium sulfate in the second coating layer: | 15.0 g (5.0% of the sodium percarbonate to be coated) |

After cooling, the coated sodium percarbonate was taken out, and no aggregate was observed.

Active oxygen of the obtained sodium percarbonate analyzed to 13.4 %.

45 This shows that there was no decomposition of the active oxygen at the coating time, and that the coating agent was coated the same as the theoretical value.
(Theoretical value : $14.4 \% \times 1 / (1 + 0.07) = 13.5 \%$)

The obtained sodium percarbonate was dissolved by 2.5 min.

Further, coated sodium percarbonate was mixed with a zeolite and detergent to investigate the storage 50 stability test. The result together with the result of the solubility rate is shown in Table 3. Formulation stability was very good, and a great improvement of stability as compared with uncoated sodium percarbonate described below was recognized.

55 EXAMPLE 12

Coated sodium percarbonate was obtained using the same procedures as in Example 11, except that potassium sulfate was used instead of sodium sulfate.

| | |
|----------------------|--|
| Sodium metasilicate: | 2.1 g (as SiO ₂ 0.7% of the sodium percarbonate to be coated) |
| Potassium sulfate: | 15.0 g (5% of the sodium percarbonate to be coated) |
| Magnesium sulfate: | 4.2 g (1.4% of the sodium percarbonate to be coated) |

5

Active oxygen of the obtained sodium percarbonate analyzed to 13.4 %.

This value shows that without decomposing sodium percarbonate at the coating time, the coating agent was coated the same as the theoretical value. Further, solubility was investigated using the same procedure as in Example 11, and it was found that the sample dissolved by 2 minutes.

10 Formulation stability was investigated in the same manner as Example 11, and it was good. The result is shown in Table 3.

EXAMPLE 13

15 Coated sodium percarbonate was obtained using the same procedures as in Example 11, except that water-glass No. 1 was used instead of sodium metasilicate, the amount of coating agent was changed, and EDTA-4Na to the sodium percarbonate particle was added (0.6% conc.) into a mixed solution of magnesium sulfate and sodium sulfate in order to stabilize the liquid.

20

| | |
|---|--|
| Water-glass No.1: | 4.5 g (SiO ₂ , 1.5 % of sodium percarbonate to be coated) |
| Sodium sulfate: | 15.0 g (5.0 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 4.2g (1.4 % of sodium percarbonate to be coated) |
| Ethylenediaminetetraacetic acid tetrasodium salt: | 0.6g (0.2 % of sodium percarbonate to be coated) |

25

30 Active oxygen of the obtained sodium percarbonate, solubility and formulation stability were investigated. The solubility was excellent, and formulation stability was good as in Example 1. The results are shown in Table 3.

EXAMPLE 14

35

12 kg of sodium percarbonate having a mean diameter of 500 µm (Active oxygen: 14.4 %) was placed on a multipore plate of a fluid drying apparatus (Fuji Paudal Co., Ltd., "MIDGET-DRYER"), then air at 3.2 m³/min was sent to make fluidization. Thereafter, by warming inlet air to from 120 to 150 °C, the temperature of the fluidizing sodium percarbonate was raised to 75 °C. After the temperature was steady at 40 75 °C, to keep it in a fluid state, a mixed solution of sodium sulfate and magnesium sulfate (sodium sulfate concentration of 15 wt%, magnesium sulfate concentration of 4.3 wt%) and an aqueous solution of sodium metasilicate (4 wt% as SiO₂) was sprayed simultaneously from a spray nozzle located 40 cm above the multipore plate, wherein 5.6 kg of the mixed solution of sodium sulfate and magnesium sulfate was sprayed at a speed of 90 g/min and 2.1 kg of the aqueous solution of sodium metasilicate was sprayed at a speed of 34 g/min, both for 62 minutes. After completion of the coating, heated air continued to be sent for 5 minutes so that the sample dried. Next, heating from the air heater finished, and the sample was cooled with a cool air flow. The temperature was controlled at from 73 to 77 °C. After cooling, the coated sodium percarbonate was removed, and no aggregate was observed.

45 The coating amount of each component as solids content was as follows:

50

| | |
|----------------------|---|
| Sodium sulfate: | 840 g (7.0% of the sodium percarbonate to be coated) |
| Sodium metasilicate: | 84 g (as SiO ₂ , 0.7% of the sodium percarbonate to be coated) |
| Magnesium sulfate: | 168 g (1.4% of the sodium percarbonate to be coated) |

55

Useful oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 3.

In the case of simultaneous spraying, the solubility and formulation stability were good, similar to the multi-spray case of Examples 11, 12 and 13.

EXAMPLE 15

5

Simultaneous spraying over 89 minutes using the same procedures as in Example 14 was conducted, except that EDTA-4Na (0.3 wt.%) to sodium sulfate particle was added into a mixed solution of sodium sulfate and magnesium sulfate, the amount of coating agent was changed, water-glass No. 1 was used instead of sodium metasilicate, and the concentration was changed.

10

| | |
|---|--|
| Sodium sulfate: | 1200 g (10.0 % of sodium percarbonate to be coated) |
| Water-glass No.1: | 84 g (as SiO ₂ , 0.7 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 240g (2.0 % of sodium percarbonate to be coated) |
| Ethylenediaminetetraacetic acid tetrasodium salt: | 24g (0.2 % of sodium percarbonate to be coated) |

15

Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated, and the results are shown in Table 3. As can be understood from Table 2, sodium percarbonate produced according to the Example of the present invention was shown to be good in solubility (necessary time for 100 % dissolution was from 2 to 2.5 minutes, i.e., fast) and good in formulation stability with detergent (after 21 days storage, only 10 % was decomposed), and had a good balance in property.

EXAMPLE 16

Coated sodium percarbonate was obtained using the same procedures as in Example 11, except that mixed aqueous solution of magnesium sulfate, sodium sulfate and sodium bicarbonate (4.2 % by weight of magnesium sulfate, 10 % by weight of sodium sulfate and 5 % by weight of sodium bicarbonate) was used instead of mixed aqueous solution of magnesium sulfate and sodium sulfate.

35

| | |
|-----------------------|---|
| Sodium meta silicate: | 2.1 g (as SiO ₂ , 0.7 % of sodium percarbonate to be coated) |
| magnesium sulfate: | 4.2 g (1.4 % of sodium percarbonate to be coated) |
| sodium sulfate: | 10.0 g (3.3 % of sodium percarbonate to be coated) |
| Sodium carbonate: | 5.0 g (1.7 % of sodium percarbonate to be coated) |

40

Active oxygen of the obtained sodium percarbonate was analyzed to 13.4 %. Further, solubility and formulation stability were investigated, and the solubility was excellent, and formulation stability was good as in Example 11. The results are shown in Table 3.

COMPARATIVE EXAMPLE 13

45

Active oxygen, solubility and formulation stability of uncoated sodium percarbonate which was used as a raw material in the present invention were investigated. The results are shown in Table 3 for comparison.

COMPARATIVE EXAMPLE 14

50

Coated sodium percarbonate was obtained using the same procedures as in Example 11, except that the spraying of the mixed solution of magnesium sulfate and sodium sulfate for the second layer was not conducted.

55

| | |
|----------------------|---|
| Sodium metasilicate: | 2.1 g (as SiO ₂ , 0.7 % of sodium percarbonate to be coated) |
|----------------------|---|

Active oxygen, solubility and formulation stability of the obtained sodium percarbonate was investigated. The results are shown in Table 3. The formulation stability was a little bit better than the uncoated sample of COMPARATIVE EXAMPLE 11, but did not show a great improvement like in EXAMPLE 1.

5 COMPARATIVE EXAMPLE 15

Coated sodium percarbonate was obtained using the same procedures as in Example 11, except that the spraying of the aqueous solution of sodium metasilicate for the first layer was not conducted.

10 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 3. The formulation stability did not show a great improvement like in Example 11.

COMPARATIVE EXAMPLE 16

15 300 g of sodium percarbonate having a mean diameter of 500 μm (active oxygen: 14.4 %) was placed on a multipore plate of a fluid dry coater (Yamato Scientific Co., Ltd., PULVIS MINI BED), then air at 0.25 m^3/min was sent to make fluidization. Thereafter, by warming inlet air, the temperature of the fluidizing sodium percarbonate was raised to 75 °C. After the temperature was steady at 75 °C, to keep it in a fluid state, 180g of an aqueous solution of magnesium chloride (10 % concentration of magnesium chloride) was sprayed from a spray nozzle located 10 cm above the multipore plate over 36 minutes at a flow rate of 5 g/min. After vacuum drying, useful oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 3. The formulation stability did not show a great improvement like in Example 11. In particular, the formulation stability with a zeolite was low, like the uncoated sample in COMPARATIVE EXAMPLE 11. Further, a great decrease of useful oxygen which was 25 over the value of dilution by the coating agent was observed.

| | |
|---|---|
| Theoretical conc. of useful oxygen: | 14.4 % \times 1 / (1 + 0.06) = 13.6 % |
| Actually measured conc. of useful oxygen: | 12.9% |

30

COMPARATIVE EXAMPLE 17

35 300 g of sodium percarbonate having a mean diameter of 500 μm (active oxygen: 14.4 %) was placed on a multipore plate of a fluid dry coater (Yamato Scientific Co., Ltd., PULVIS MINI BED), then air at 0.25 m^3/min was sent to make fluidization. Thereafter, by warming inlet air, the temperature of the fluidizing sodium percarbonate was raised to 50 °C. After the temperature was steady at 50 °C, to keep it in a fluid state, 150 g of an aqueous solution of a mixed salt of sodium carbonate and sodium sulfate (8.6 % concentration of sodium carbonate, 11.2 % of sodium sulfate) was sprayed from a spray nozzle located 10 cm above the multipore plate over 30 minutes at a flow rate of 5 g/min. For 10 minutes after spray completion, only gas at the same temperature continued to be sent, and drying was completed. Then, the gas was changed to cool wind, and the sample was cooled to 30 °C. Then, the coated sodium percarbonate was removed from the apparatus, and little aggregates were observed.

40

| | |
|-------------------|--|
| Sodium sulfate: | 16.8 g (5.6 % of sodium percarbonate to be coated) |
| Sodium carbonate: | 13.2 g (4.4 % of sodium percarbonate to be coated) |

50 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 3. Formulation stability did not show a great improvement like in Example 11.

COMPARATIVE EXAMPLE 18

55 Coated sodium percarbonate was obtained using the same procedures as in Example 6, except that after forming the first coating layer, without using sodium sulfate, the second coating layer was formulated using only an aqueous solution of magnesium sulfate.

| | |
|---|--|
| Sodium metasilicate (SiO_2): | 2.1 g (0.7 % of sodium percarbonate to be coated) |
| Magnesium sulfate: | 19.2 g (6.4 % of sodium percarbonate to be coated) |

5 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 3.

COMPARATIVE EXAMPLE 19

10 Coated sodium percarbonate was obtained using the same procedures as in Example 6, except that after forming the first coating layer, without using magnesium sulfate, the second coating layer was formulated using a mixed aqueous solution of sodium sulfate and sodium carbonate.

| | |
|---|--|
| Sodium metasilicate (as SiO_2): | 2.1 g (0.7 % of sodium percarbonate to be coated) |
| Sodium sulfate: | 15.0 g (5.0 % of sodium percarbonate to be coated) |
| Sodium carbonate: | 4.2 g (1.4 % of sodium percarbonate to be coated) |

15 Active oxygen, solubility and formulation stability of the obtained sodium percarbonate were investigated. The results are shown in Table 3.

Table 3

| | EXAMPLE | | | | | | COMPARATIVE EXAMPLE | | | | | | |
|-------------------------|---------|-----|-----|-----|-----|-----|---------------------|-----|-----|-----|-----|-----|-----|
| | 11 | 12 | 13 | 14 | 15 | 16 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
| Solubility (min.) | 2.0 | 2.0 | 2.5 | 2.5 | 2.5 | 2.5 | 1.5 | 3.5 | 1.5 | 5.0 | 1.5 | 4.0 | 3.0 |
| Storage Stability 1 (%) | 95 | 91 | 93 | 95 | 96 | 96 | 30 | 50 | 79 | 43 | 48 | 68 | 72 |
| Storage Stability 2 (%) | 91 | 89 | 90 | 92 | 93 | 95 | 50 | 54 | 68 | 75 | 55 | 72 | 70 |

25 While the invention has been described in detail and with reference to specific embodiments, it will be apparent to one skilled in the art that changes and modifications can be made therein without departing from the spirit and scope thereof.

30 The features disclosed in the foregoing description or in the claims may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

Claims

- 40 1. A stabilized sodium percarbonate particle comprising a sodium percarbonate particle having at least one coating layer thereon, wherein the at least one coating layer comprises:
- (a) a silicate;
 - (b) magnesium sulfate; and,
- 45 2. A stabilized sodium percarbonate particle according to Claim 1, wherein the silicate is selected from the group consisting of sodium orthosilicate, sodium metasilicate and water-glass.
3. A stabilized sodium percarbonate particle according to Claim 1, wherein the coated sodium percarbonate particle comprises a mixture of a wet powdery sodium percarbonate particle and a recovered sodium percarbonate particle which partially contains a coating agent component.
- 50 4. A stabilized sodium percarbonate particle according to Claim 1, wherein the silicate is coated on the sodium percarbonate in an amount of from 0.01 mole to 0.06 mole based on SiO_2 per mole of sodium percarbonate.

5. A stabilized sodium percarbonate particle according to Claim 1, wherein the magnesium sulfate is coated on the sodium percarbonate in an amount of from 0.006 mole to 0.06 mole based on SiO₂ per mole of sodium percarbonate.
- 10 6. A stabilized sodium percarbonate particle according to Claim 1, wherein a chelating agent is contained in the at least one coating layer.
7. A stabilized sodium percarbonate particle according to Claim 1, wherein the alkali metal salt is an alkali metal carbonate.
- 15 8. A stabilized sodium percarbonate particle according to Claim 7, wherein the alkali metal carbonate is sodium carbonate.
9. A stabilized sodium percarbonate particle according to Claim 1, wherein a mixed solution of an alkali metal carbonate and a silicate is sprayed and dried to form a first coating layer, then an aqueous solution of magnesium sulfate is sprayed and dried to form a second coating layer.
- 20 10. A stabilized sodium percarbonate particle according to Claim 7, wherein the at least one coating layer is a coating layer formed by spraying (a) a mixed aqueous solution of an alkali metal carbonate and a silicate, and (b) an aqueous solution of magnesium sulfate on the sodium percarbonate particle simultaneously using different nozzles and drying.
- 25 11. A stabilized sodium percarbonate particle according to Claim 7, wherein the at least one coating layer is a coating layer formed by spraying (a) an alkali metal carbonate, (b) a silicate, and (c) an aqueous solution of magnesium sulfate on the sodium percarbonate particle simultaneously using different nozzles and drying.
- 30 12. A stabilized sodium percarbonate particle according to Claim 7, wherein the alkali metal carbonate is coated on the sodium percarbonate particle in an amount of from 0.075 mole to 0.18 mole per mole of sodium percarbonate.
- 35 13. A stabilized sodium percarbonate particle according to Claim 7, wherein the silicate and the alkali metal carbonate are coated on the sodium percarbonate particle in amounts such that the coating amount of the silicate is from 0.05 to 0.8 times the coating amount of the alkali metal carbonate on a molar basis.
- 40 14. A stabilized sodium percarbonate particle according to Claim 7, wherein the magnesium sulfate and the alkali metal carbonate are coated on the sodium percarbonate particle in amounts such that the coating amount of the magnesium sulfate is from 0.03 to 0.8 times the coating amount of the alkali metal carbonate on a molar basis.
- 45 15. A stabilized sodium percarbonate particle according to Claim 1, wherein the alkali metal salt is an alkali metal bicarbonate.
16. A stabilized sodium percarbonate particle according to Claim 15, wherein the alkali metal bicarbonate is sodium bicarbonate.
- 50 17. A stabilized sodium percarbonate particle according to Claim 15, wherein an aqueous solution of a silicate is sprayed and dried to form a first coating layer, then a mixed aqueous solution of magnesium sulfate and an alkali metal bicarbonate is sprayed and dried to form the second coating layer.
- 55 18. A stabilized sodium percarbonate particle according to Claim 15, wherein the at least one coating layer is formed by spraying (a) an aqueous solution of silicate, and (b) a mixed aqueous solution of magnesium sulfate and an alkaline metal bicarbonate on the sodium percarbonate particle simultaneously using different nozzles and drying.
19. A stabilized sodium percarbonate particle according to Claim 15, wherein the at least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, (b) an aqueous solution of magnesium sulfate, and (c) an alkali metal bicarbonate on the sodium percarbonate particle simulta-

neously using different nozzles and drying.

20. A stabilized sodium percarbonate particle according to Claim 15, wherein the alkali metal bicarbonate is coated on the sodium percarbonate particle in an amount of from 0.05 mole to 0.25 mole per mole of sodium percarbonate.
5
21. A stabilized sodium percarbonate particle according to Claim 15, wherein the silicate and the alkali metal bicarbonate are coated on the sodium percarbonate particle in amounts such that the coating amount of the silicate is from 0.04 to 1.2 times the coating amount of the alkali metal bicarbonate on a molar basis.
10
22. A stabilized sodium percarbonate particle according to Claim 15, wherein the magnesium sulfate and the alkali metal bicarbonate are coated on the sodium percarbonate particle in amounts such that the coating amount of the magnesium sulfate is from 0.024 to 1.2 times the coating amount of the alkali metal bicarbonate on a molar basis.
15
23. A stabilized sodium percarbonate particle according to Claim 1, wherein the alkali metal salt is an alkali metal sulfate.
20
24. A stabilized sodium percarbonate particle according to Claim 23, wherein the alkali metal sulfate is sodium sulfate.
25
25. A stabilized sodium percarbonate particle according to Claim 23, wherein an aqueous solution of a silicate is sprayed and dried to form a first coating layer, then a mixed aqueous solution of magnesium sulfate and alkali metal sulfate is sprayed and dried to form a second coating layer.
30
26. A stabilized sodium percarbonate particle according to Claim 23, wherein the at least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, and (b) a mixed aqueous solution of magnesium sulfate and an alkali metal sulfate on the sodium percarbonate particle simultaneously using different nozzles and drying.
35
27. A stabilized sodium percarbonate particle according to Claim 23, wherein the at least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, (b) an aqueous solution of magnesium sulfate, and (c) an alkali metal sulfate on the sodium percarbonate particle simultaneously using different nozzles and drying.
40
28. A stabilized sodium percarbonate particle according to Claim 23, wherein the alkali metal sulfate is coated on the sodium percarbonate particle in an amount of from 0.05 mole to 0.2 mole per mole of sodium percarbonate.
45
29. A stabilized sodium percarbonate particle according to Claim 23, wherein the silicate and the alkali metal sulfate are coated on the sodium percarbonate particle in amounts such that the coating amount of the silicate is from 0.05 to 1.2 times the coating amount of the alkali metal sulfate on a molar basis.
50
30. A stabilized sodium percarbonate particle according to Claim 23, wherein the magnesium sulfate and the alkali metal sulfate are coated on the sodium percarbonate particle in amounts such that the coating amount of the magnesium sulfate is from 0.03 to 1.2 times the coating amount of the alkali metal sulfate on a molar basis.
55
31. A stabilized sodium percarbonate particle according to Claim 23, wherein an alkali metal bicarbonate is added as a coating agent.
32. A stabilized sodium percarbonate particle according to Claim 31, wherein the alkali metal bicarbonate is sodium bicarbonate.
33. A stabilized sodium percarbonate particle according to Claim 31, wherein an aqueous solution of a silicate is sprayed and dried to form a first coating layer, then a mixed aqueous solution of magnesium sulfate, an alkali metal sulfate and an alkali metal bicarbonate is sprayed and dried to form a second

coating layer.

34. A stabilized sodium percarbonate particle according to Claim 31, wherein the at least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, and (b) a mixed aqueous solution of magnesium sulfate, an alkali metal sulfate and an alkali metal bicarbonate on the sodium percarbonate particle simultaneously using different nozzles and drying.
5
35. A stabilized sodium percarbonate particle according to Claim 31, wherein the at least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, (b) an aqueous solution of magnesium sulfate, (c) an alkali metal sulfate, and (d) an alkali metal bicarbonate on the sodium percarbonate particle simultaneously using different nozzles and drying.
10
36. A stabilized sodium percarbonate particle according to Claim 31, wherein the alkali metal sulfate is coated on the sodium percarbonate particle in an amount of from 0.05 mole to 0.2 mole per mole of sodium percarbonate, and the alkali metal bicarbonate is coated on the sodium percarbonate in an amount of from 0.04 mole to 0.17 mole per mole of sodium percarbonate.
15
37. A stabilized sodium percarbonate particle according to Claim 31, wherein the silicate and the alkali metal sulfate are coated on the sodium percarbonate particle in amounts such that the coating amount of the silicate is from 0.05 to 1.2 times the coating amount of the alkali metal sulfate on a molar basis.
20
38. A stabilized sodium percarbonate particle according to Claim 31, wherein the magnesium sulfate and the alkali metal sulfate are coated on the sodium percarbonate particle in amounts such that the coating amount of the magnesium sulfate is from 0.03 to 1.2 times the coating amount of the alkali metal sulfate on a molar basis.
25
39. A stabilized sodium percarbonate particle according to Claim 31, wherein the alkali metal bicarbonate and the alkali metal sulfate are present in amounts such that the amount of the alkali metal bicarbonate is from 0.2 to 0.85 times the amount of the alkali metal sulfate on a molar basis.
30
40. A method for preparing a stabilized sodium percarbonate particle, which comprises:
spraying on a sodium percarbonate particle:
(a) an aqueous solution of magnesium sulfate;
(b) an aqueous solution of a silicate; and
35 (c) an aqueous solution of an alkali metal salt selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates and alkali metal sulfates; wherein two of the aqueous solutions can be combined in the form of a mixed solution; and drying to form at least one coating layer on the sodium percarbonate particle.
41. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the temperature of the sodium percarbonate during spray drying is from 40 to 95 °C.
40
42. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the aqueous solution of a silicate contains from 0.5 to 9 wt% of a silicate as SiO₂.
45
43. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the aqueous solution of magnesium sulfate contains magnesium sulfate in a concentration of from 0.2 to 25 wt%.
44. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein a mixture of a wet powdery sodium percarbonate particle and a recovered sodium percarbonate particle which partially contains a coating agent component is used to form the coated sodium percarbonate particle.
50
45. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the sodium percarbonate particle to be coated has a diameter of from 300 to 3000 µm.
55

46. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein a chelating agent is added in an aqueous solution of a coating agent.
47. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein a
5 mixed solution of an alkali metal carbonate and a silicate is sprayed and dried to form a first coating layer, then an aqueous solution of magnesium sulfate is sprayed and dried to form a second coating layer.
48. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the at
10 least one coating layer is a coating layer formed by spraying (a) a mixed aqueous solution of an alkali metal carbonate and a silicate, and (b) an aqueous solution of magnesium sulfate on the sodium percarbonate particle simultaneously using different nozzles and drying.
49. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the at
15 least one coating layer is a coating layer formed by spraying (a) an aqueous solution of an alkali metal carbonate, (b) an aqueous solution of a silicate, and (c) an aqueous solution of magnesium sulfate on the sodium percarbonate particle simultaneously using different nozzles and drying.
50. A method for preparing a stabilized sodium percarbonate particle according to Claim 47 or Claim 48,
20 wherein the mixed aqueous solution contains from 5 to 20 wt% of an alkali metal carbonate and 0.5 to 9 wt% of a silicate as SiO_2 , and wherein the aqueous solution of magnesium sulfate contains from 3 to 25 wt% of magnesium sulfate.
51. A method for preparing a stabilized sodium percarbonate particle according to Claim 49, wherein the
25 aqueous solution of an alkali metal carbonate has a concentration from 3 to 15 wt% of an alkali metal carbonate, the aqueous solution of silicate has a concentration of 0.5 to 9 wt% of a silicate as SiO_2 , and the aqueous solution of magnesium sulfate has a concentration from 3 to 25 wt% of magnesium sulfate.
52. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein an
30 aqueous solution of a silicate is sprayed and dried to form a first coating layer, then a mixed aqueous solution of magnesium sulfate and an alkali metal bicarbonate is sprayed and dried to form a second coating layer.
53. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the at
35 least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, and (b) a mixed aqueous solution of magnesium sulfate and an alkali metal bicarbonate on the sodium percarbonate particle simultaneously using different nozzles and drying.
54. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the at
40 least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, (b) an aqueous solution of magnesium sulfate, and (c) an aqueous solution of an alkali metal bicarbonate on the sodium percarbonate particle simultaneously using different nozzles and drying.
55. A method for preparing a stabilized sodium percarbonate particle according to Claim 52 or Claim 53,
45 wherein the aqueous solution of a silicate has a concentration of 0.5 to 9 wt% of a silicate as SiO_2 , and wherein the mixed aqueous solution has a concentration of from 0.2 to 15 wt% of magnesium sulfate and a concentration of from 3 to 9 wt% of an alkali metal bicarbonate.
56. A method for preparing a stabilized sodium percarbonate particle according to Claim 52 or Claim 53,
50 wherein the aqueous solution of a silicate has a concentration of 0.5 to 9 wt% of a silicate as SiO_2 , and the mixed aqueous solution has a concentration of from 0.2 to 15 wt% of magnesium sulfate and concentration of from 3 to 10 wt% of an alkali metal bicarbonate.
57. A method for preparing a stabilized sodium percarbonate particle according to Claim 52 or Claim 53,
55 wherein nitrilotriacetic acid, ethylenediaminetetraacetic acid or a salt thereof is added in the mixed aqueous solution of magnesium sulfate and an alkali metal bicarbonate.

58. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein an aqueous solution of a silicate is sprayed and dried to form a first coating layer, then a mixed aqueous solution of magnesium sulfate and an alkali metal sulfate is sprayed and dried to form a second coating layer.
- 5 59. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the at least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, and (b) a mixed aqueous solution of magnesium sulfate and an alkali metal sulfate on the sodium percarbonate particle simultaneously using different nozzles and drying.
- 10 60. A method for preparing a stabilized sodium percarbonate particle according to Claim 40, wherein the at least one coating layer is a coating layer formed by spraying (a) an aqueous solution of a silicate, (b) an aqueous solution of magnesium sulfate, and (c) an aqueous solution of an alkali metal sulfate on the sodium percarbonate particle simultaneously using different nozzles and drying.
- 15 61. A method for preparing a stabilized sodium percarbonate particle according to Claim 58 or Claim 59, wherein the aqueous solution of a silicate has a concentration of 0.5 to 9 wt% of a silicate as SiO₂, and wherein the mixed aqueous solution has a concentration of from 0.2 to 25 wt% of magnesium sulfate and a concentration of from 3 to 20 wt% of an alkali metal sulfate.
- 20 62. A method for preparing a stabilized sodium percarbonate particle according to Claim 60, wherein the aqueous solution of a silicate has a concentration of 0.5 to 9 wt% of a silicate as SiO₂, the aqueous solution of magnesium sulfate has a concentration from 0.2 to 25 wt% of magnesium sulfate, and the aqueous solution of an alkali metal sulfate has a concentration from 3 to 20 wt% of an alkali metal sulfate.
- 25 63. A method for preparing a stabilized sodium percarbonate particle according to Claim 58 or Claim 59, wherein the mixed aqueous solution of magnesium sulfate and an alkali metal sulfate further comprises an alkali metal bicarbonate.
- 30 64. A method for preparing a stabilized sodium percarbonate particle according to Claim 60, wherein the aqueous solution of an alkali metal sulfate further comprises an alkali metal bicarbonate to form a mixed aqueous solution.
- 35 65. A method for preparing a stabilized sodium percarbonate particle according to Claim 63, wherein the aqueous solution of a silicate has a concentration of 0.5 to 9 wt% of a silicate as SiO₂, and the mixed aqueous solution of has a concentration from 0.2 to 15 wt% of magnesium sulfate, a concentration from 3 to 12 wt% of an alkali metal sulfate, and a concentration from 0.5 to 6 wt% of an alkali metal bicarbonate.
- 40 66. A method for preparing a stabilized sodium percarbonate particle according to Claim 64, wherein the aqueous solution of a silicate has a concentration of 0.5 to 9 wt% of a silicate as SiO₂, the aqueous solution of magnesium sulfate has a concentration from 0.2 to 25 wt% of magnesium sulfate, and the mixed aqueous solution has a concentration from 3 to 12 wt% of alkali metal sulfate and a concentration from 0.5 to 6 wt% of alkali metal bicarbonate.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 7149

| DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim |
| A | DE-A-26 22 610 (INTEROX) * page 2, paragraph 2 - page 6, paragraph 5 * * claims * --- | 1,2,4, 7-9,12, 17, 23-25, 28, 40-42, 47, 50-52, 55,56, 58,61,62 |
| D,A | FR-A-2 424 228 (KAO SOAP CO., LTD.) * page 3, line 28 - page 5, line 3 * * claims 1-7 * --- | 1,5,9, 17,25 |
| D,A | FR-A-2 226 460 (INTEROX) * page 1, line 26 - page 2, line 9 * * page 2, line 34 - page 4, line 8 * * table 1 * * claims 1,5-10 * --- | 1,7-9, 15-17, 23-25, 40,41, 47,52,58 |
| A | EP-A-0 405 797 (TOKAI DENKA KK) * page 1, line 24 - page 2, line 9 * * examples 5-7,9 * * claims 1-3,5 * ----- | 1,3,5, 7-9,12, 15-17, 20, 23-25, 28,31-33 |
| The present search report has been drawn up for all claims | | |
| Place of search | Date of completion of the search | Examiner |
| THE HAGUE | 11 August 1994 | Van der Poel, W |
| CATEGORY OF CITED DOCUMENTS | | |
| X : particularly relevant if taken alone | T : theory or principle underlying the invention | |
| Y : particularly relevant if combined with another document of the same category | E : earlier patent document, but published on, or after the filing date | |
| A : technological background | D : document cited in the application | |
| O : non-written disclosure | L : document cited for other reasons | |
| P : intermediate document | & : member of the same patent family, corresponding document | |